

Nanoparticles-assisted MSIS-MP-AES hydride generation determination of As and Sb

M. T. Kiryakova, E. K. Varbanova, K. K. Simitchiev, V. J. Kmetov*

*Department of Analytical Chemistry and Computer Chemistry,
University of Plovdiv "Paisii Hilendarski", 24 Tzar Assen Str.4000 Plovdiv, Bulgaria*

Received November 16, 2018; Revised December 17, 2018

For the first time hydride generation (HG) in the presence of silica-coated $\text{MnFe}_2\text{O}_4@\text{SiO}_2$ magnetic nanoparticles (MNPs) was tested. A benefit of adding inert and easily recyclable (collected from the waste by a permanent magnet) MNPs into the reaction cell - Multi Mode Sample Introduction System (MSIS®) was expected, namely by providing expanded contact surface and improving the gas-liquid separation, to extend the potential of microwave plasma atomic emission spectrometry (MP-AES) to determine As and Sb at sub-ppb levels. It was found that the suggested approach does not contribute to sensitivity changes for As or for Sb, but more than twice improves the measurement precision for both elements. The addition of 1.6 mg ml^{-1} MNPs into the 1.5 % NaBH_4 leads to smooth and steady reagent flow supply due to a diminishing of hydrogen bubbles formation in the delivery tubing. Therefore, a stable equilibrium of the input-output analyte mass transfer can be maintained, even working at extremely high for MSIS sample and hydride reagent flows (15 ml min^{-1} and 7.5 ml min^{-1} , respectively). A sensitivity enhancement for As in presence of alcohols was found and attributed to a carbon-related matrix effect, therefore 2% ethanol was added to the NaBH_4 . The proposed nanoparticles assisted hydride generation approach extends the ability of MSIS-MP-AES and allows determination of As and Sb with instrumental LODs of 0.17 ppb and 0.05 ppb respectively, which are much lower than those in other recently published works.

Keywords: microwave plasma atomic emission spectrometry (MP-AES), nanoparticles, hydride generation, MSIS, As, Sb, trace elements analysis

INTRODUCTION

Microwave Plasma Atomic Emission Spectrometry (MP-AES) is a relatively new technique, which works with nitrogen sustained plasma (N_2 gas could be extracted from the air) and does not require flammable or expensive gases. The method provides several analytical benefits as: fast multielement consecutive measurements in a large linear dynamic range. The microwave plasma is cooler than the widely used inductively coupled plasma (ICP), which works with argon gas flows. Another difference is that the microwave applied power in MP-AES instruments is fixed (i.e. 1000 W) and cannot be changed. For that reason, the temperature of MP discharge cannot be instrumentally controlled, hence the sensitivity of the recorded emission signals could be optimised only by variations of N_2 nebulization gas flow, sample flow and the viewing position of the plasma [1, 2]. It was proved [3, 4] that the MP-AES detection limits (LOD) are compatible to those of Flame Atomic Absorption Spectrometry (FAAS), but are not so low as in ICP-OES. The limitation of MP-AES to detect trace elements at low concentrations in environmental samples have been

reported in [5]. European legislation postulates maximum acceptable concentrations (MAC) of total Sb and As of 5 and $10 \mu\text{g L}^{-1}$, respectively, for waters for human consumption and natural waters [6, 7]. These levels are much below the detection limits of MP-AES if conventional nebulisation is used [5].

A well-known approach for improving the analytical potential of atomic spectrometry analysis is the so called *hydride generation technique* (HG), applicable for elements such as As, Se, Sb, Bi, Te, Sn, Ge, Pb, which can form volatile hydrides by chemical reaction with a hydride donor reagent (most often NaBH_4). The important advantages of HG are: i) fast separation of the analytes in gaseous form from the liquid, allowing complex matrix analyses, i.e. high dissolved solids sample solutions and even suspensions (which cannot be nebulized); ii) the generated volatile hydrides can be easily and efficiently transported to the plasma by a carrier gas; iii) less solvent is loaded in the plasma source, which prevents its cooling; iv) enables work with much higher sample flows compared to the nebulization mode, ensuring significantly higher mass transfer of the analytes.

In a specially dedicated monography [8], Dedina

* To whom all correspondence should be sent.

E-mail: kmetov@uni-plovdiv.bg

M. T. Kiryakova et al.: Nanoparticles-assisted MSIS-MP-AES hydride generation determination of As and Sb and Tsalev describe the instrumental and chemical parameters that have to be considered for HG procedure optimisation. The important ones are: sample acidity; sample volume and amount/concentration of NaBH₄; analyte oxidation state/pre-reduction; carrier gas flows; chemical reaction temperature; reaction/collection time. In HG, the total mass fraction of the analyte delivered in the atomizer depends on two major parameters - sample flow rate and carrier gas flow rate and these variables are specific for individual instrumental setup [9].

The use of a new commercial Multi Mode Sample Introduction System (MSIS®) in HG mode enables up to 100 times lowering of LODs for the target hydride-forming elements in comparison to conventional nebulisation [10, 11]. In MSIS® the sample solution and hydride generation reagent (HGR) react in a thin film onto a rough – surfaced cone, which provides good reagents mixing and fast gas-liquid separation. The advantages of using MSIS® in HG mode are described in [12].

The combination MSIS-HG-MP-AES is quite new and still not enough explored. Very recent papers about the analytical applications of this instrumental setup are given in [13-15]. Total As analysis in Californian wines is presented in [13]; multielemental determination of As, Bi, Ge, Sb, and Sn in agricultural samples is reported in [14]; determination of As and Se in mineral waters is described in [15].

Nanoparticles can be used as a trapping sorbent, for selective separation and preconcentration of analytes prior to spectrometric determination [16, 17]. Silica-coated MnFe₂O₄@SiO₂ magnetic nanoparticles synthesized in our laboratory showed good magnetic properties and have been used for magnetic supported micro dispersive solid phase extraction [18]. The MNPs protected by silica coating are stable and could be reused several times [18].

The present work aims to explore the possibility of the above-mentioned relatively inert MNPs to act as surface expansion and gas-liquid separation supporting media in combination with MSIS-HG-MP-AES. The goal was, working with this combination, to extend the potential of the method to determine As and Sb in sub-ppb levels. To the best of our knowledge, this is the first time when such approach is used.

EXPERIMENTAL

Instrumentation

All analyses were performed with an Agilent 4200 MP-AES spectrometer equipped with Agilent

4107 nitrogen generator; Agilent MSIS® was used only in HG mode (the unused sample line to the nebulizer was blocked). Other used equipment was as follows: External peristaltic pump – Gilson, Minipuls 2; ER10 stirrer; delivery tubing: purple/black 2.29 mm i.d, connected to the top of the MSIS® for hydride generation reagent; blue/blue 1.65 mm i.d, attached to the MSIS® bottom for sample solution delivery tubing; black/white 3.18 mm i.d. for waste tubing; permanent magnet: Disc magnet S-45-30-N, Ø 45 mm, height 30 mm, Supermagnete (Uster, Switzerland)

Reagents and standard solutions

All reagents and solvents were of analytical grade. MnFe₂O₄@SiO₂ nanoparticles were synthesized in our laboratory according to the procedure described in [18]. The used reagents in the study were: L-cysteine powder 98%, Acros Organics; sodium borohydride powder 98%, Acros Organics; CH₃OH 99.8%, Merck; C₂H₅OH 99.9%, Rai-him; i-C₃H₇OH, Chimtex Ltd, Dimitrovgrad; Na₂CO₃ 95.8%, Valerus; standard solutions: As (III) 100 mg L⁻¹ in 0.5% NaOH 0.1% NaCl, CPAchem; As(V) 100 mg L⁻¹ in H₂O, CPAchem; Sb 100 mg L⁻¹ 99.99% in 2% HNO₃, 0.5% HF CPAchem, HCl 35.9%, Rai-him; double distilled water (BDW).

Sample preparation

Stock standard solutions of As or Sb 100 mg L⁻¹ were diluted with 0.1 mol L⁻¹ HCl to desired working concentrations. L-cysteine was added to a final concentration of 0.5% m/v. The solution was incubated for 60 min (room temperature). Hydride generation reagent (HGR) contains 1.5% NaBH₄ and 0.1% NaOH, prepared by dissolving NaBH₄ in appropriate BDW volume, followed by addition of NaOH to 0.1% final concentration. Stirrer was used to maintain the homogeneity in the case of MNPs addition.

RESULTS AND DISCUSSION

Optimisation of the operating conditions

The MSIS-MP-AES instrumental setup was optimised for HG determination of As and Sb by using model solutions. A set of characteristic emission lines for both analytes (Table 1) was tested in order to select free from spectral interference wavelengths with best sensitivity and good precision.

The MP-AES instrumental parameters were optimised in respect of maximum signal-to-noise ratio. The working parameters are given in Table 2.

L-cysteine was used as non-toxic pre-reducing agent, which was found efficient to increase

M. T.Kiryakova et al.: Nanoparticles-assisted MSIS-MP-AES hydride generation determination of As and Sb sensitivity at low acid concentration [19, 20]. Hydrochloric acid was used as acidic medium, in which the oxidation states of As(III) and Sb(III) are sustained. Experimentally it was proved that working with 0.5% of L-cysteine in the presence of HCl with concentration (0.06 - 0.2 mol L⁻¹) leads to equalization of HG sensitivity for both As(III) and As(V).

Table 1. MP-AES tested emission lines

Analyte	Line, nm	Type	Relative intensity
As	188.979	I	582
As	193.695	I	1307
As	228.812 ^a	I	1731
Sb	206.833	I	1487
Sb	217.581	I	2827
Sb	231.147	I	3841

^a Spectral interference from Cd was observed

Table 2. MP-AES working parameters

Plasma viewing position	0
Integrated pump speed, (rpm)	80
Read time, s	5
Sample uptake time, s	10
Stabilization time, s	20
Number of replicates	5
Background correction	Off-peak, left + right

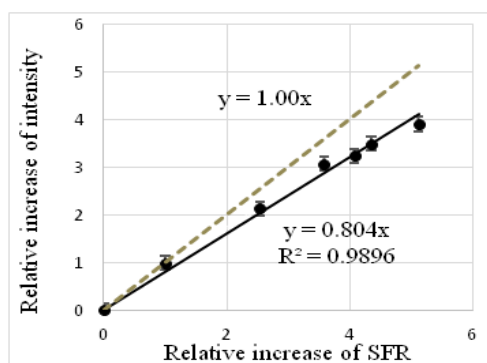


Fig. 1. Relative enhancement of emission intensity (50 ppb As 193.695 nm) vs relative increase of SFR.

The effect of sample and carrier gas flow rates on the emission intensity of As (193.695 nm) was studied, and it was found that there is no interaction between the two variables. It was proved that the sample flow rate (SFR) has much greater effect than that of the N₂ carrier with optimal gas flow rate of 0.6 L min⁻¹. Using further multivariate optimization by central composite design, the following optimal values for MSIS working conditions were found: i) NaBH₄ concentration - 1.5 % m/m; ii) SFR - 15 mL min⁻¹; and iii) ratio of

reagent (NaBH₄)-to-sample flow rates - 1:2 i.e. NaBH₄ flow rate - 7.5 mL min⁻¹.

In order to facilitate the work with SFR above 11 mL min⁻¹ the original MSIS chamber was modified by widening the diameter of the sample entrance aperture to 1.2 mm. For efficient draining of the huge volume of liquid phase entering the chamber (15 mL min⁻¹ SFR + 7.5 mL min⁻¹ HGR), it was necessary to use two channels of the integrated peristaltic pump and to install two waste tubings (3.18 mm i.d.) connected with T-junction to the drainage orifice of the MSIS chamber. In order to ensure independent variation of HGR flow rate, an external Gilson peristaltic pump was used with separate control.

Close to straight line relationship between the recorded emission intensities and the sample amount pumped into the MSIS cell was derived for SFR in the range 2 - 15 mL min⁻¹. This indicates that the efficiency of signal production is not deteriorated at higher sample flow rates, despite of working with flows much higher than recommended by the manufacturer. From Fig. 1, obtained by plotting the calculated relative enhancements of emission intensities vs the relative SFR increases, it is evident that some part (~20%) of the analyte introduced into the MSIS chamber is not utilised (the slope in Fig. 1 is 0.804 instead of the optimal 1.00). The reason for this could be an incomplete hydride formation chemical reaction, due to ineffective mixing of sample and HGR or other kinetic limitations.

Effect of MNPs

It is worthwhile to investigate whether the addition of MNPs to the HGR could increase the efficiency of the chemical reaction by providing higher contact surface into the MSIS cell and improving gas-liquid separation. For this purpose, a mixture of HGR solution with silica-coated magnetic nanoparticles (MnFe₂O₄@SiO₂) was pumped from the top of MSIS. Emission signals for As (193.695, 188.979 and 228.812 nm) and Sb (217.581, 231.147 nm) were measured, varying the MNPs concentrations into the HGR. The results were compared with those without addition of MNPs. The first tests showed no effect in sensitivity for Sb lines and a prominent sensitivity enhancement (13-25%) in emission signals for all As lines in the presence of freshly prepared MNPs (~2 mg ml⁻¹). The used MNPs were collected from the waste by means of a permanent magnet, rinsed by BDW and reused with no memory effect observed. Surprisingly, the commented enhancement effect on As signals was lost working with recycled MNPs. Repetitive experiments

showed restored sensitivity enhancement only if MNPs were previously washed with ethanol. The explanation for this unexpected behavior could be that the signal enhancement is a result of the presence of alcohol, carried by freshly synthesized nanoparticles (see the synthetic procedure in [18]). This explanation was afterwards proved by the same results obtained from both experiments - using recycled MNPs (~2 mg ml⁻¹) rinsed with ethanol and by working without MNPs, but adding 2% ethanol in HGR instead. An important conclusion is that introduction of MNPs in the MSIS reaction cell does not contribute to sensitivity changes neither for As nor for Sb. Evidently, the hydride generation procedure in the MSIS reactor design runs with enough efficiency, hence provision of extra surface or better mixing is not required even at these extremely high sample and reagent flows.

On the other hand, it was visually observed that the presence of MNPs into the HGR solution reduces bubbles formation in delivery tubing and significantly improves the stability of NaBH₄. This phenomenon resulted in smooth and steady reagent flow supply and is beneficial for maintaining a dynamic equilibrium of the input-output mass transfer into the reaction chamber. The use of easily recyclable MNPs could be appointed as a green analytical approach. The commented stabilization effect of MNPs reflects in improving the precision of MSIS-HG-MP-AES measurements of both hydride forming elements tested. This is proved by the results presented in Table 3 which summarises the pooled standard deviation for signals of As and Sb. The MNPs supported HG shows more than twice improvement in the precision irrespective from the alcohol presence.

Table 3. Improvement of the measurement precision of the registered intensities of As (193.695 nm) and Sb (217.581 nm)

No of consec. measurement	As				Sb			
	HGR ^a		HGR/MNPs/ C ₂ H ₅ OH ^b		HGR ^a		HGR/MNPs ^c	
	I, c s ⁻¹	(SD), c s ⁻¹	I, c s ⁻¹	(SD), c s ⁻¹	I, c s ⁻¹	(SD), c s ⁻¹	I, c s ⁻¹	(SD), c s ⁻¹
1	248	(11)	302	(6)	759	(33)	779	(11)
2	241	(23)	303	(11)	767	(47)	778	(17)
3	254	(15)	296	(14)	763	(16)	770	(25)
4	240	(8)	294	(5)	797	(55)	772	(9)
5	239	(22)	292	(6)	774	(21)	780	(14)
6	265	(19)	299	(10)	789	(45)	769	(9)
7	241	(24)	299	(10)	804	(64)	755	(10)
8	243	(14)	298	(10)	757	(13)	757	(5)
9	229	(14)	297	(5)	799	(45)	754	(13)
10	241	(16)	294	(5)	760	(15)	772	(6)
Sum	2441	(164)	2974	(82)	7769	(353)	7687	(118)
pooled RSD	7%		2.8%		5%		1.5%	

Conditions: 2 ppb As or 1 ppb Sb in 0.1 mol L⁻¹ HCl and 0.5% L-cysteine.

^a Only HGR (solution of 1.5% NaBH₄/0.1% NaOH) was used; ^b HGR with addition of 1.6 mg ml⁻¹ MNPs and 2% C₂H₅OH; ^c HGR with addition of 1.6 mg ml⁻¹ MNPs.

By varying MNPs concentration from 0.4 to 6 mg ml⁻¹ in HGR with 2% C₂H₅OH, a robust stabilisation effect was found if the content of MNPs is kept between 1 - 2 mg ml⁻¹. For HGR solution with above 3 mg ml⁻¹ MNPs the precision was deteriorated because of the increased viscosity of the HGR solution. All further experiments have been performed with 1.6 mg ml⁻¹ MNPs. Effect of carbon-containing compounds.

The commented above sensitivity enhancement for As in presence of alcohol could be explained by a carbon-related matrix effect, which has been already confirmed for ICP-AES and ICP-MS

measurements of As in the presence of C [21– 23]. Despite this the effect of the carbon in HG-MSIS-MP-AES analysis has not been reported in the literature before. The mass fraction of carbon transported to the excitation source can be monitored by C emission signal at λ=193.045 nm. This spectral line is close to the emission of As at 193.695 nm, and both lines can be recorded by MP-AES in the same spectral window. Additional experiments performed by us showed signal enhancement for As depending on the physico-chemical characteristics of the carbon containing

M. T. Kiryakova et al.: Nanoparticles-assisted MSIS-MP-AES hydride generation determination of As and Sb solutions used in combination with MSIS-HG-AES. The results are presented in Table 4.

Table 4. Carbon emission intensity and signal enhancement for 10 ppb As for HGR with additives

HGR + additives	C _{193.045nm} , I c s ⁻¹	AS 193.695 nm signal enhancement, %
Non	-	-
CH ₃ OH	23269	13±1.1
C ₂ H ₅ OH	39682	20±2
i-C ₃ H ₇ OH ^a	86561	11±2
i-C ₃ H ₇ OH+NP _s	89275	20±1.8
0.05% NaCO ₃	4881	7±0.6
0.1% NaCO ₃	7816	8±0.5
0.6% NaCO ₃	25062	9±0.7
1.2% NaCO ₃	64166	6±0.9

^a Visual observation of foam generation

Table 5. Instrumental detection limits compared to those from recent papers.

	LOD, ppb, MSIS-MP-AES-HG	
	From the literature	Modified MSIS HGR/MNP _s /C ₂ H ₅ OH (current work)
As	0.38 [13]	0.17
	0.48 [14]	
	10 [15]	
Sb	0.48 [14]	0.05

The sensitivity gain was greater for C₂H₅OH and it could be preferred as a less toxic agent. The gas-liquid separation in the MSIS chamber could be troubled if the viscosity of the reaction mixture is increased. In the case of i-C₃H₇OH, foam generation in the MSIS cell arises, but by adding 1.6 mg ml⁻¹ of MNPs less foaming is observed and as a result a gain in sensitivity for As was found (Table 4). Additional studies are required to explain these observations and to investigate the application of MNPs as an antifoaming agent in HG.

CONCLUSIONS

An effective technique for generation of hydrides of As, Sb by using a commercial (MSIS®) cell combined with nitrogen microwave plasma atomic emission spectrometry (MP-AES) was developed. A modification in (MSIS®) enables work with high reagents flow rates. At this conditions the addition of inert and easily recyclable magnetic nanoparticles to the hydride reagent do not improve the HG reaction efficiency, but leads to significant stabilization effect of the hydride generation reagent delivery and more than twice precision improvement. Sensitivity enhancement for As was confirmed in a presence of carbon carrying agents.

The proposed nanoparticles assisted hydride generation approach extends the ability of MSIS-MP-AES to determine sub-ppb levels of As and Sb.

Acknowledgment: The work was supported by NSF Project DN19/9 2018-2020 (INISA). The authors would like to thank T.E.A.M. Ltd. and Agilent Technologies for kindly providing Agilent 4200 MP-AES instrumentation to the Department of Analytical Chemistry and Computer Chemistry at University of Plovdiv "P. Hilendarski".

REFERENCES

1. D. Gonçalves, T. McSweeney, G. Donati, *J. Anal. At. Spectrom.*, **31**, 24, (2016).
2. N. Chalyavi, P. S. Doidge, R. J. S. Morrison, G. B. Partridge, *J. Anal. At. Spectrom.*, **32**, 1988, (2017).
3. M. Wiedenbeck, L. Bedard, R. Bugoi, M. Horan, K. Linge, S. Merchel, L. Morales, D. Savard, A. Souders, P. Sylvester, DOI: 10.1111/j.1751-908X.2014.00347.x, *Geostand. Geoanalytical Res.*, **38**, 467, (2014).
4. Agilent Technologies, Application eHandbook, 2016, p. 5
5. S. Karlsson, V. Sjöberg, A. Ogar, *Talanta*, **135**, 124, (2015).
6. COMMISSION DIRECTIVE 2003/40/EC, *Regulation*, **2**, 30 (2003).
7. "COUNCIL DIRECTIVE 98/83/EC," (1998).
8. J. Dedina, D. Tsalev, Hydride Generation Atomic Absorption Spectrometry, John Wiley & Sons Ltd., Chichester, 1995.
9. J. Dedina, Generation of Volatile Compounds for Analytical Atomic Spectroscopy, R.A. Meyers (ed.), *Encyclopedia of Analytical Chemistry*, **S1-S3**, 897, John Wiley & Sons Ltd., Chichester, 2011.
10. A. Asfaw, G. Wibetoe, *J. Anal. At. Spectrom.*, **21**, 1027, (2006).
11. M. Ślachciński, *Appl. Spectrosc. Rev.*, **49**, 271, (2014).
12. I. D. Brindle, *Patent*, US 2003 / 0230712 A1, **1**, (2003).
13. C. K. Tanabe, H. Hopfer, G. Gilleland, A. Liba, S. E. Ebeler, J. Nelson, *J. Anal. At. Spectrom.*, **31**, 1223, (2016).
14. R. C. Machado, C. D. B. Amaral, J. A. Nóbrega, A. R. Araujo Nogueira, *J. Agric. Food Chem.*, **65**, 4839, (2017).
15. I. V. Mikheev, E. A. Karpukhina, L. O. Usol'tseva, T. O. Samarina, D. S. Volkov, M. A. Proskurnin, *Inorg. Mater.*, **53**, 1422, (2017).
16. H. Ahmad, A. Ahmad, S. S. Islam, *Microchim. Acta*, **184**, 2007, (2017).
17. A. Dados, E. Papparizou, P. Eleftheriou, C. Papastephanou, C. D. Stalikas, *Talanta*, **121**, 127, (2014).

18. D. Georgieva, V. Stefanova, V. Kmetov, I. Roman, N. Kovachev, A. Canals, *Univ. Plovdiv „Paisii Hilendarski“ – Bulg. Sci. Pap.*, **38**, 7, (2011), https://blogs.uni-plovdiv.net/argon/files/2011/09/001_NT38_2011.pdf
19. H. Chen, I. D. Brindle, X. chun Le, *Anal. Chem.*, **64**, 667, (1992).
20. B. Welz, M. Sucmanova, *Analyst*, **118**, 1425, (1993).
21. H. Wiltsche, M. Winkler, P. Tirk, *J. Anal. At. Spectrom.*, **30**, 2223, (2015).
22. G. Grindlay, L. Gras, J. Mora, M. T. C. De Loos-Vollebregt, *Spectrochim. Acta Part B At. Spectrosc.*, **115**, 8, (2016).
23. T. Nakazawa, D. Suzuki, H. Sakuma, N. Furuta, *J. Anal. At. Spectrom.*, **29**, 1299, (2014).